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Strain-Induced Crystallization of Isotactic Polystyrene from the Glassy and "Rubbery" States

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In a continuing effort to extend our understanding of the strain-induced crystallization mechanism we have examined the morphology of oriented isotactic polystyrene (IPS) crystallized from the glassy and "rubbery" states under a variety of experimental conditions (elongation, annealing temperature and time, and sample geometry) by means of a wide variety of experimental techniques using Au decorations, solvent etching, electron diffraction, and bright- and dark-field electron microscopy. The oriented morphology is found to be strongly dependent on the original strained state and other experimental variables; it can be either lamellar, fibrillar, or a combination of the two. A fine texture is found to exist in both the lamellar and fibrillar crystals. Extended-chain line nuclei were also sought. Our results, including dark-field studies of highly stretched samples and samples which have been Au decorated or elutriated with solvent, do not reveal any crystallites of length greater than about 100 Å along the stretch direction, thus essentially ruling out their presence in IPS crystallized under strain. The observations are in complete agreement with the strain-induced crystallization mechanism suggested by Yeh and can also account for such phenomena as stress decay and melting temperature increase.

I. INTRODUCTION

Polymer fibers and films are important commercial products. The major contribution to their commercial importance is the strength of these materials which is a result of their oriented crystal morphology that is brought about by the stretching and the subsequent (and/or concurrent) crystallization processes. Traditionally, the oriented crystallites in fibers or films were thought to be due to a two-step process involving first, a parallel alignment of chain segments due to the stretching process and second, an additional parallel-chain alignment in the stretch direction during the subsequent crystallization, resulting in a bundle or fringed-micellar-type morphology. This traditional view of nucleation and growth of crystallites in the oriented state was used in Flory's theory¹ to account for phenomena such as the stress decay as a function of crystallization time and for the increase in melting temperature of the resulting oriented crystallites. Gent's observations of stress decay and melting-point rise in crosslinked *cis*-1, 4-polyisoprene,² *trans*-polychloroprene,³ and *trans*-1, 4-polyisoprene⁴ were interpreted as proof for this traditional view of bundlelike crystallization in oriented polymers.

However, numerous morphological studies showed

that the dominant morphology of polymers, including crosslinked polyethylene⁵ and natural rubber,^{6,7} when crystallized under strain consists of rows of perpendicularly oriented chain-folded lamellas. The chain folding would predict a stress rise rather than the often observed stress decay during oriented crystallization. A stress rise has been reported by Gent⁴ to occur during oriented crystallization of *trans*-1, 4-polyisoprene (balata) for extensions less than about 100% and this has been attributed by him to be evidence for the formation of chain-folded crystals at these low extensions. We have observed well-defined lamellas and obtained a small-angle meridional periodicity from *trans*-1, 4-polyisoprene after crystallization in the stretched state at elongations well above 100% and up to 400–500%.⁸ This would predict a stress rise during the oriented crystallization, but experimental studies by Gent showed otherwise.

Keller and Machin proposed a two-step mechanism for formation of row-oriented lamellas.⁵ It involved the formation of fibrillar crystals which they suggested consisted essentially of extended chains resulting from the stretching process, and followed subsequently during the growth step by the formation of chain-folded lamellas onto the fibrillar nuclei. They further suggested that the

formation of extended-chain crystals during the nucleation process should provide an explanation for the well-known stress-decay phenomenon, and that the formation of chain-folded crystals during the growth process should provide another explanation for the stress rise. However, the stress rise as predicted by their proposed mechanism never occurs in natural rubber during the formation of chain-folded lamellas at all elongations or in balata at elongations greater than 100%, suggesting that the stress rise may have a different origin.

There is also some question concerning the structure of the proposed nuclei as being essentially extended chains. Dark-field studies^{9,10} of suitably prepared specimens often showed that *c*-axis-oriented crystallites seldom extend more than 100–200 Å in the stretch direction. X-ray line-broadening studies by Buchanan and Miller¹¹ of oriented isotactic polystyrene gave a value of 85–100 Å from careful analysis of the meridional 102 reflection. However, many of these studies were carried out on specimens which have seldom been stretched more than 300–400%. It is possible that the detection of extended-chain nuclei may be greatly hampered by the presence of the more abundant chain-folded crystals. Therefore, in order to establish the presence or absence of extended-chain fibrillar crystals, one must employ suitable specimens, preferably those that have been crystallized in a highly stretched state and therefore have fewer, or possibly no, lamellar-type crystals present.

We have chosen isotactic polystyrene (IPS), in addition to the others we have studied, for the purpose of clarifying many of the above-mentioned problems regarding the nucleation and the growth processes of crystallites in the oriented state. Isotactic polystyrene is chosen because, like the other candidates, polyethylene terephthalate⁹ and natural rubber,⁶⁻⁸ it has a very slow crystallization rate. Its reported maximum crystal growth rate in the unoriented state is of the order of 0.1–1 μ/min at 180–190 °C.¹² Consequently it is possible to study the various stages of crystal growth under carefully chosen crystallization conditions. Unfortunately thin films of IPS are limited to extensions less than 100% at room temperature. For extensions greater than 100% we have used IPS plasticized with a suitable amount (40%) of benzophenone, thus bringing its glass transition temperature to well below room temperature or about –2 °C.¹³ Therefore the plasticized IPS is now in a rubbery state at room temperature and can be stretched easily to extremely high elongations (>600%). In this study, both the glassy IPS and the plasticized rubbery IPS were used in order to give us a direct comparison of the morphology of ori-

ented crystallites obtained from the two different states. We have also taken into consideration the effects of various crystallizing conditions (crystallizing in the absence of a substrate vs crystallizing in the presence of a substrate, various annealing temperatures and times) and sample geometry (film vs fiber) in addition to the effects of elongations which other investigators have generally considered with respect to the changes observed in oriented morphology. We have used primarily bright-field and dark-field electron microscopy and electron diffraction to study thin films crystallized under strain. Specimens examined include those which have been platinum shadowed and gold decorated or mildly etched with amyl acetate in order to remove the noncrystallized regions and expose the crystallites.

II. EXPERIMENTAL

Thin films of Dow IPS (viscosity × average molecular weight, $M\eta = 550\,000$) were cast from a 0.4% benzene solution either directly onto a Mylar substrate and stretched uniaxially using a small home-made extensometer; or onto a glass slide after which the film, upon drying, was floated off onto the surface of distilled water and stretched uniaxially using a pair of modified draftsman's dividers.⁹ After stretching, the films were annealed at 155 or 175 °C for times between 1 and 20 min and afterwards prepared for electron microscope studies. A few stretched films were also annealed unsupported on a microscope grid for comparison with those which were annealed in contact with a Mylar substrate.

The plasticized rubbery thin films were cast onto glass slides from 0.4% solutions of IPS/benzophenone (60/40) in benzene made by pipetting together proper ratios of 0.4% IPS and 0.4% benzophenone in benzene solutions. The plasticized thin films as prepared gave a pure amorphous IPS diffraction pattern with no observable rings due to benzophenone. After floating off onto the surface of water, thin films about 1200 Å thick were most successful in stretching to fairly uniform elongations ranging between 100 and 600% by means of the draftsman's dividers. After transfer to microscope grids, the stretched films were annealed at 125, 155, or 175 °C for times between 1 and 60 min. A few films were stretched on Mylar using the small home-made stretcher and then annealed while the stretched films were still in contact with Mylar substrate.

The stretched films were prepared for electron microscopy in a manner similar to the method developed earlier; they were either shadowed with platinum⁹ or decorated with gold.^{14,15} Some were

also etched mildly with amyl acetate prior to platinum shadowing. The method for selective etching, similar to that used by Padden and Keith,¹⁶ involved mounting stretched thin films on pieces of freshly cleaved mica and crystallizing the films in the same manner as before. After crystallization, the pieces of mica were plunged into a bath of amyl acetate, at 23 °C, for times normally ranging from 10 to 60 sec, thoroughly drained, and then air dried. Other solvents such as xylene, acetone, and methyl ethyl ketone were also tried at various temperatures and etching times. However room-temperature amyl acetate was found to be the most suitable because it did not cause any solvent-induced crystallization in the noncrystalline regions nor did it cause any substantial alteration to the crystallites because of the nature of the mild etching process.

The electron microscopes used were JEM 5A and a Phillips 200 with resolutions of better than 15 Å. Dark-field microscopy was done using both a movable-aperture technique as well as a tilted-beam technique for high-resolution studies: The dark-field exposure times varied between 10 and 60 sec, depending on the specimen and the beam current.

III. RESULTS

The observed morphologies were found to depend greatly on the various factors investigated, namely, sample geometry, degree of elongation, annealing temperature and time, and annealing conditions. Very often the observed changes were contributed not just by one, but by a combination of these factors, making interpretations rather difficult. However, by keeping some of the variables as nearly constant as possible, for example, by preparing specimens from the same stretched film and crystallizing them at the same temperature but varying the crystallization time, we were able to show the effect of time on the change in morphology.

A. Annealing Temperature and Time

After stretching to various elongations (greater than 100% for the plasticized system), oriented IPS's showed little or no crystallinity according to their diffraction patterns. This was somewhat unexpected for the plasticized "rubbery" system, since natural rubber crystallizes readily upon stretching in the rubbery state. One possible explanation may lie in the molecular-chain flexibility difference between the two polymers. Annealing is necessary to effect any observable signs of crystallinity in these oriented systems of IPS. As expected, the rate and extent of crystallization were greatly affected by the crystallization (annealing) temperature and time for a given elongation, as

judged by the surface area covered by the crystallites. The crystal thickness increased with crystallization temperature. For example, oriented IPS (with or without plasticizer) crystallized at 155 °C and 175 °C resulted in crystal thickness measuring 140 and 150 Å, respectively. These values correspond reasonably well with the small-angle x-ray long periods of 137 and 157 Å reported by Manley and Blais¹⁷ for unoriented IPS crystallized at 156 and 176 °C, respectively.

The crystal thickness did not appear to depend on annealing time nor on elongation, but the extent of crystallization does. For a given elongation and annealing temperature, longer annealing times resulted in an increase in extent of crystallization, but the increase appeared to be contributed both by the formation of additional new crystallites and the growth of existing crystallites (see Figs. 1, 2, and 5).

B. Pure IPS Crystallized in the Oriented Glassy State

Thin films of glassy amorphous IPS stretched to 50–100% and crystallized either at 155 or 175 °C developed a lamellar morphology with the lamellas oriented nearly perpendicular to the stretch direction. An example is shown in Fig. 1 which was obtained from a film stretched to 100% and annealed at 175 °C for 20 min while in contact with a Mylar substrate. It showed a great deal of lamella twisting. By comparison, less twisted lamellas were observed, if the stretched film was annealed unsupported on a microscope grid, suggesting a definite effect of substrate on the crystal arrangement. The effect of substrate on the degree of lamella twisting was also noted earlier in polyethylene terephthalate.⁹

Additional features of the morphology were made clear by Au decoration and solvent etching. First,

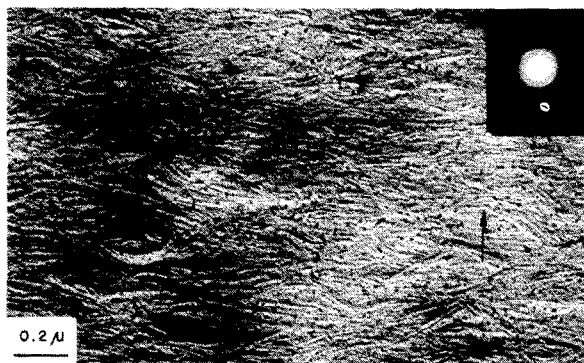


FIG. 1. Glassy IPS stretched 100% and annealed at 175 °C for 20 min on Mylar, platinum shadowed. Stretch direction is indicated by the arrow in this and all subsequent pictures.

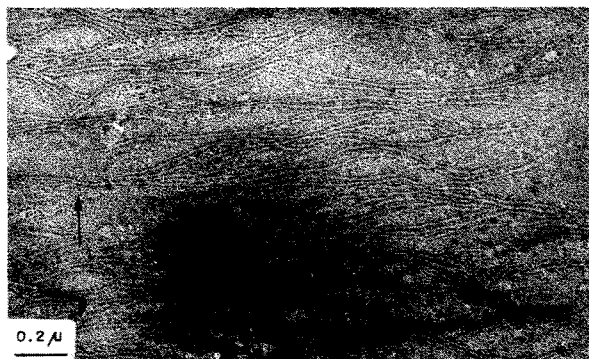


FIG. 2. Glassy IPS stretched 100% and annealed at 175 °C for 5 min on Mylar, Au decorated.

the presence of a lamellar structure is very distinct in samples which have been either Au decorated^{18,19} or solvent etched (Figs. 2 and 3). Figure 2 also shows that there is no observable Au-voided region of any extended length in the direction of stretch. Since we have established^{18,19} that the crystalline region tends to be voided by Au, this observation suggests to us that there are probably no extended-chain crystals present in these specimens. However, many of the lamellas do seem to be attached to one another in various randomly located places, probably by tie molecules holding the lamellas together at these contact points. This suggestion finds strong support from careful studies of the solvent-etched specimens (Fig. 3).

The effects of selective etching of the uncrystallized region by amyl acetate for two different washing times, 20 and 60 sec, are illustrated in Fig. 3. The amount of noncrystalline material removed by the solvent is directly dependent on the washing time. At shorter washing times, only the surface layer, consisting mainly of noncrystallizable material such as low molecular weight and the atactic fraction of IPS, was preferentially removed. This was followed by increasing removal of the noncrystalline regions inbetween the crystallites at longer washing times, until finally only individual crystalline lamellas, many of which were seen held together by tie molecules, were left. By comparison of the crystallites in etched and unetched specimens, it was concluded that the very mild amyl acetate did not appreciably alter the size or the shape of crystallites.

Solvent etching revealed several other features that were undetected or detected barely in unetched, platinum-shadowed, or gold-decorated specimens. One feature is the presence of mosaic-type structures in the lamellas. The lateral dimension of these mosaic structures appears rather constant, of the order of the lamella thickness. They can-

not be due to any artifacts introduced during solvent etching, since the solvent used is extremely mild, nor can they be attributed to any debris left behind after the washing step as indicated by the absence of such structures in the surface region surrounding the lamellas. Some debris can be seen in Fig. 3(b) after longer etching time, but they are clearly due to portions of mosaic structures which have been accidentally broken off from the lamellas during handling of the specimen or during the etching. The presence of these mosaic structures is therefore real as in polyethylene terephthalate.⁹

Corresponding electron diffraction patterns (e.g., see inset in Fig. 1) of areas shown in Figs. 1–3 indicate that the molecular-chain axis is mainly parallel to the stretch direction and therefore perpendicular to the lamellas, thus requiring a majority of the chains except for a few tie molecules to be folded within individual lamellas. The fairly sharp equatorial reflections and the relatively broad $10\bar{2}$ reflections agree well with the corresponding crystal dimensions observed in the electron micrographs.

C. Plasticized IPS Crystallized to the Oriented "Rubbery" State

Elongations between 100 and 400% - Lamellar Morphology

Under comparable experimental conditions at low elongations, plasticized IPS crystallized in the rubbery state showed a lamellar morphology very similar to that seen in IPS crystallized in the glassy state. Annealing plasticized IPS on a Mylar substrate again introduced an increased degree of lamella twisting similar to that observed in Fig. 1 as compared to a sample annealed in the absence of a substrate (Fig. 4). Since twisting tends to mask the details that may be present within or in between the lamellas, it was decided to concen-

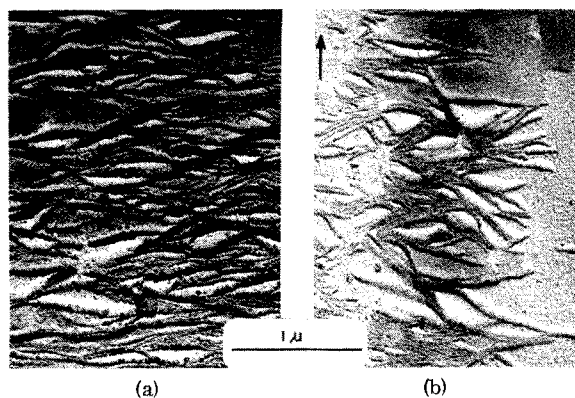


FIG. 3. Glassy IPS stretched 100% and annealed at 175 °C for 20 min at 175 °C, solvent etched for (a) 20 sec and (b) 60 sec.

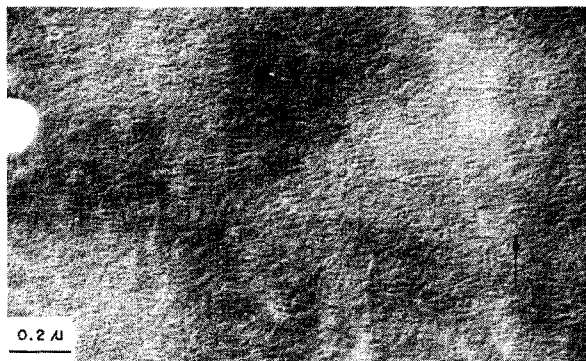


FIG. 4. Plasticized IPS stretched 100% and annealed at 155°C for 2 min, platinum shadowed.

trate our studies on samples that were annealed directly on the microscope grid, i. e., in the absence of a substrate. This also allows us to compare studies made earlier on stretched thin films of polyethylene terephthalate⁹ and the more recent studies on natural rubber,⁸ which were carried out under similar crystallization conditions.

When crystallized at 300%, the observed crystalline structures are extremely similar to those lamellar structures reported by Andrews⁶ in stretched thin films of natural rubber crystallized at low temperatures and by Yeh⁷ in crosslinked natural rubber strain crystallized at room temperature for comparable extensions. These lamellas give the

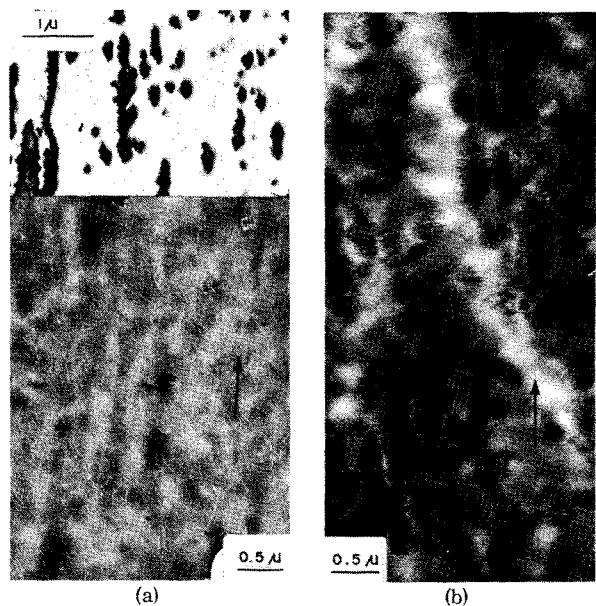


FIG. 5. Plasticized IPS stretched 300%, annealed at 125°C for (a) 4 min and (b) 6 min, platinum shadowed. Inset in (a) shows the complete removal of dense (darker) regions by etching a similar specimen shown in (a) in solvent for 60 sec.

appearance that they have nucleated along some lines parallel to the stretch direction (Fig. 5). However, careful examinations of solvent-etched and gold-decorated specimens, including those stretched to high elongations (Fig. 6), did not reveal line nuclei with diameters greater than about 15 Å, which was the limit of our resolution. This conclusion was also supported by dark-field results, which agreed with the findings of Klement and Geil on IPS.¹⁰

Another interesting feature which is worth noting is the appearance of numerous patches of dense (and/or diffracting) regions over the surface during the early stages of crystallization [Figs. 5(a) and 5(b)]. They probably result from some type of preordering of chain segments prior to the formation of lamellas appearing in the same vicinity. Such regions were absent in as-stretched specimens prior to annealing, ruling out the possibility of any phase separation occurring upon stretching. A similar densification was also noted in various regions of pure IPS prior to lamellar crystallization in the unoriented state.²⁰ However, these pre-ordered regions, unlike the lamellas, are still very susceptible to solvent attack. This is often seen by the removal of these dense regions upon complete solvent etching [see inset in Fig. 5(a)], leaving behind matured crystalline lamellas.

Another interesting observation is that the lamellas formed in these more highly stretched specimens (300–400%) also have a greater tendency to adhere to one another [compare inset in Fig. 5(a) with Fig. 3(b)], suggesting the presence of numerous tie molecules in between these lamellas, more than in between those in the less-stretched sample (100%).

Figure 7 shows typical examples of electron diffraction patterns obtained from plasticized samples

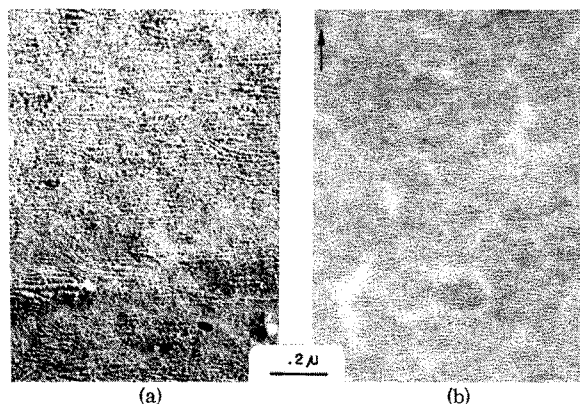


FIG. 6. Plasticized IPS stretched 400% and annealed at 155°C for 6 min; (a) solvent etched and (b) decorated.

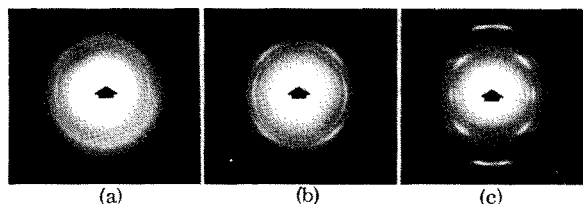


FIG. 7. Electron diffraction patterns of plasticized IPS: (a) stretched 100%, annealed at 155°C for 2 min, (b) stretched 100% and annealed at 155°C for 6 min, and (c) stretched 300% and annealed at 125°C for 20 min.

stretched between 100 and 400% and annealed at three different temperatures for various times between 1 and 60 min. The results agree well with the morphologies observed in the micrographs. For example, longer annealing times [compare Figs. 7(a) and 7(b)] show an increase in intensity (due to greater crystallinity) as well as an increase in the sharpness of the equatorial reflections (due to increase in the lateral dimensions of the lamellas and/or perfection of crystallites). Increasing elongations [see Figs. 7(b) and 7(c)] resulted in a splitting of the $10\bar{2}$ reflection and a decrease in arcing of the equatorial reflections (due to lamellas becoming increasingly more perpendicular to the stretch direction). The $10\bar{2}$ reflection, however, remained very broad in all the electron diffractions that were examined including those obtained from samples which had extensions greater than 600% (see Fig. 9).

Elongations between 500 and 600% – Fibrillar Morphology

With increasing elongation, the tendency of lamella formation becomes less until finally a morphology consisting entirely of fibrils is obtained at extensions greater than 600%. At about 500% several lamellas were seen mixed in with some very fine fibrils (Fig. 8). The lamellas have limited lateral dimensions, generally less than about 500 Å. The diameter of the fibrils is about 200 Å and they contribute to the substantial increase in the broadening of the equatorial reflections (Figs. 8 and 9).

There are other features in the figure which need to be pointed out. First, there is again the presence of finer structures within the lamellas, but these fine structures are present along the fibrils as well. The size of these fine structures is about the same in both morphologies, but their packing is obviously different. In the fibrils the structures appear to orient in strings along the stretch direction, whereas in the lamellas they are arranged along the crystal dimension and therefore perpendicular to the stretch direction. Second, many of the lamellas are void of any fibrillar nuclei. Third,

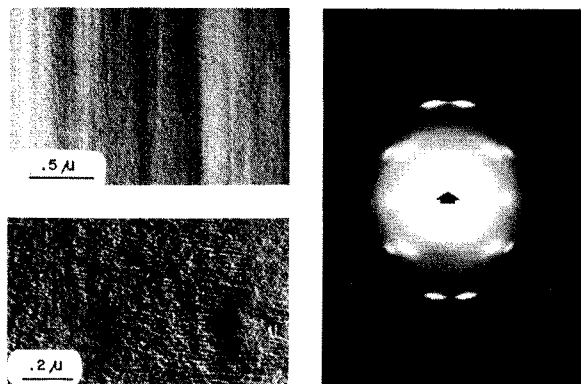


FIG. 8. Plasticized IPS stretched 500% and annealed at 125°C for 60 min, solvent etched for 40 sec. The electron diffraction was obtained from a similar area shown on the left.

many of the fibrils are seen in isolated locations; while others can be seen intermingled but not with any particular relationship to the neighboring lamellar structures. Fourth, both the lamellas and the fibrils are extremely resistant to solvent attack, suggesting the presence of increasingly more tie molecules, especially within the fibrillar crystals.

Figure 9 shows an electron micrograph obtained from a highly stretched film ($\geq 600\%$) which had undergone some lateral contraction. The general appearance is extremely fibrillar and resembles the fibrillar morphology one generally sees in a uniaxially oriented fiber.

As seen in Figs. 8 and 9 the fibrils appear to have a finer texture within them. To prove this observation, numerous dark-field micrographs were

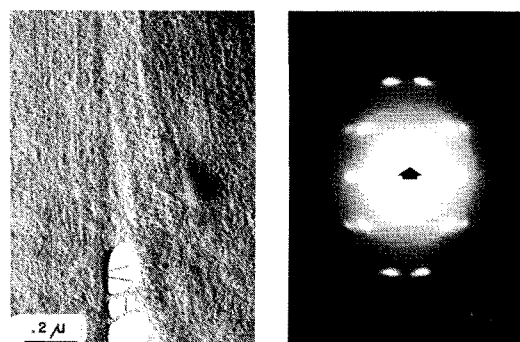


FIG. 9. Plasticized IPS stretched to about 600% and annealed at 175°C for 6 min, platinum shadowed. The film has contracted laterally after the high stretching and has also split a little along the stretch direction. The electron diffraction was obtained from a similar area shown on the left.

taken using the $10\bar{2}$ reflection. An example of this is shown in Fig. 10; none of the diffracting regions measure more than 100–200 Å in any one direction, particularly, the one along the stretch direction. In some instances there is a slight suggestion of a faint thread (20 Å) running through the crystallites, but the over-all impression of the dark-field micrograph is peppery and very similar to the ones seen in highly drawn polyethylene.²¹

IV. DISCUSSION

The appearance of lamellas at low elongations and of fibrils at high elongations in crystallized IPS is consistent with the gross morphology of many other oriented polymers when crystallized under similar conditions. However, there are several important findings resulting from the present investigation which may provide additional information towards our current understanding concerning the morphology and the mechanism of strain-induced crystallization. These include (a) the presence of a finer structure *within* the lamellas and the fibrils, (b) the absence of extended-chain crystals, at least of those with diameters greater than about 20 Å and lengths greater than about 75–150 Å along the *c* axis, (c) coexistence of lamellas and fibrils with no apparent relation to one another, (d) decreasing tie molecules between lamellas with decreasing elongations, (e) increasing lamella twisting with decreasing elongations and/or increasing relaxation of the oriented polymer (in particular, the effect brought about by the substrate during annealing), (f) possible preordering in the initial state of crystallization, and (g) substantial increase in the number of crystallites in addition to growth of existing crystallites as a function of

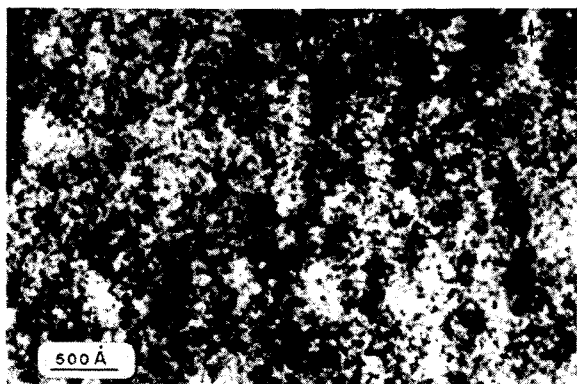


FIG. 10. Dark-field micrograph obtained from plasticized IPS stretched to greater than 500% and annealed at 155 °C for 6 min, platinum shadowed. It was taken using the meridional $10\bar{2}$ reflection.

crystallization time in the stretched state. The findings (d) and (e), and (f) and (g) are probably related to each other.

It is of interest to note that several of the findings [in particular under findings (a), (b), (e), and (f)] made in this study have also been reported in conjunction with studies carried out on strain-induced crystallization from the glassy state. For example, fine structures in the form of nodules and evidence for limited crystal growth in the stretch direction have been reported by Yeh and Geil in polyethylene terephthalate⁹ and by Klement and Geil in polycarbonate, polymethyl methacrylate, as well as polystyrene.¹⁰ Since all of these studies were made on polymers that were crystallized from the glassy state, any direct comparisons between the results on them and those on polyethylene⁵ and natural rubber^{6,7} crystallized from the rubbery state will have to be made with some reservations. In this study we have made an attempt to bridge this gap by studying oriented IPS crystallized from both the glassy and the rubbery states, and concluded from the observations that there is very little difference, if any, between the two. The conclusion is also supported by our current studies on natural rubber⁸ which showed many of the same observations listed earlier under (a)–(c).

It is gratifying to learn that the basic morphology of oriented polymers is rather similar regardless of the polymer and/or the state from which the oriented polymer is crystallized, the basic morphology being lamellar at low elongations and fibrillar at high elongations and that both the lamellas and fibrils contain a similar fine texture. The obvious question is: Why? The answer probably lies in the morphology of the amorphous state, which has recently been shown²⁰ to be very similar in both the glassy and the rubbery states, being composed of 30–100-Å nodular grains containing partially ordered chain segments imbedded in a medium of randomly coiled chains.

Yeh⁷ has suggested a two-step strain-induced crystallization process involving both a nucleation and a growth step, which differs from the one proposed by Keller and Machin.⁵ It is based primarily on experimental evidence. The strain-induced nucleation step is due to the orientation in the direction of stretch of nodular grains present in the amorphous state. Additional thermal treatment may be necessary to bring about crystallization of chain segments, primarily within the grains, during the nucleation step. The crystal growth occurs during thermal treatment by additional crystallization of neighboring nodules and/or a rearrangement of crystallized nodules. Consequently, either

lamellas or fibrils may form depending on the conditions (elongation, annealing temperature, etc.) under which the polymer is crystallized. (The suggested mechanism is very similar to the recrystallization of cold-drawn polyethylene which begins with microfibrils containing mosaic crystal blocks and, after annealing, results in chain-folded lamellas.^{21,22})

Since folds, albeit irregular, are suggested²⁰ to be initially present within the nodular grains, any additional chain folding that may occur during the growth may be only a small fraction of the total. This may explain why stress never rises in natural rubber in the extended state, but always decreases as a result of an increasing number of chain segments becoming parallel to the stretch direction during the subsequent crystallization process, provided that there is no imposed strain on the tie molecules between the nodules in the stretch direction. When the tie molecules between the nodules become strained, e.g., by lamella twisting, as observed at low extensions, then stress rise may occur. The stress rise in polyethylene and gutta percha at low extensions is probably caused more by the increased lamella twisting at low extensions than by the chain-folding process that has been previously suggested by Keller and Machin.⁵

We would also like to offer an alternative explanation for the observed melting point increase with increasing extensions, since the evidence presented in this paper has essentially ruled out the presence of extended-chain crystals in oriented polymers. We suggest that the melting point increase is mainly caused by the increasing number of the molecules under strain at high extensions. The strained tie molecules can impose a restraint on the randomization of the crystallized chain segments. A similar suggestion has been made by Kawai, Ebara, and Maeda²³ to explain the high-melting differential thermal analysis (DTA) shoulder reported for stirred crystallized solution-grown "shish-kabobs". The presence of extended-chain crystals in "shish-kabobs" has also been recently ruled out by Krueger and Yeh based on dark-field studies.¹⁹

V. CONCLUSION

In this paper we have shown that the lamellar and fibrillar crystals in oriented IPS both consist of finer structures, about 100 Å in size. The major difference between the two morphologies, aside from their obvious difference in shape, lies in the number of tie molecules which the two morphologies contain; it is appreciably larger in the more highly oriented state than the less oriented state.

The observations made in this study can be readily accounted for by the two-step strain-induced crys-

tallization mechanism suggested earlier by Yeh⁷ but not the one proposed by Keller and Machin.⁵ Phenomena such as stress relaxation and/or stress increase during the secondary crystal-growth process and the melting point increase for strain-induced crystallites can also be explained based on the observed morphology and the suggested strain-induced crystallization mechanism.

The usefulness of thin-film studies to the understanding of oriented morphology is also demonstrated in the present study. Suitably prepared thin films which have been Au decorated and/or solvent etched have brought clear additional features which may have escaped unnoticed in untreated specimens.

ACKNOWLEDGMENTS

The authors wish to thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for the support of this work.

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